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WPI Abstract Accession No:71-04536S/03 &  
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(54) Imide nucleating agents for polymers

(57) A polymeric composition comprises at least one polymeric material and at least one nucleating agent selected from a group consisting of specified imide compounds. More particularly a process is provided to improve the degree of crystallinity, the crystallization onset temperature and/or the mechanical properties of polymeric materials. The use of the specified imides as nucleating agents for polymeric materials as well as to compositions, such as masterbatches and liquid concentrates, comprising said imide compounds is described.

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(WPAT)

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|-------|---------------|----------|
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|       | DE19520262-A1 | 95.12.14 |
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| PNA - | J08012809     |          |

GB 2 290 296 A

## NUCLEATING AGENTS

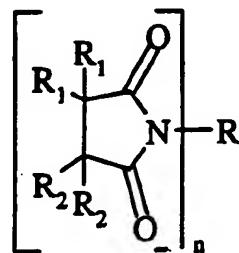
The invention relates to a polymeric composition comprising at least one polymeric material and at least one nucleating agent selected from the group consisting of compounds of formulae I to VIII.

More particularly the invention relates to a process to enhance the degree of crystallinity, the crystallization onset temperature, and the mechanical properties of polymeric materials. The invention relates further to the use of special imide compounds according to formulae I to VIII as nucleating agents for polymeric materials as well as to compositions, e. g. masterbatches and liquid concentrates comprising said imide compounds.

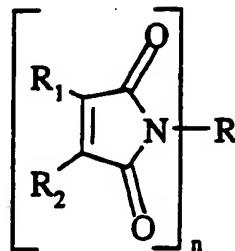
The physical properties which are improved by these nucleating agents (hereinafter called NA), are for example, crystallization temperature and/or mechanical properties like tensile strength or elongation at break.

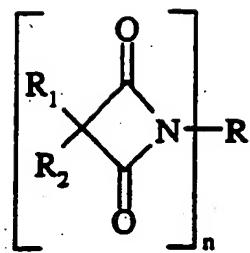
According to the invention, there is provided a polymeric composition comprising a polymeric material and a nucleating agent of formulae I to VIII

(I)

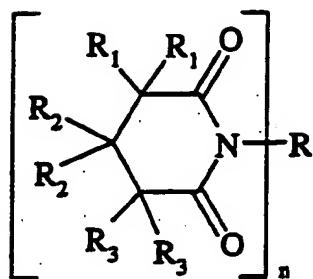


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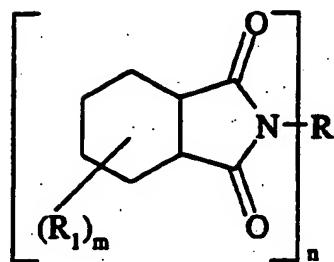




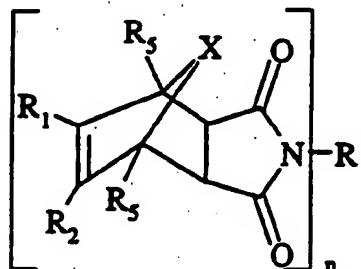
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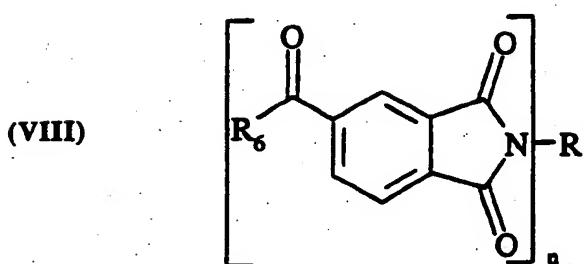
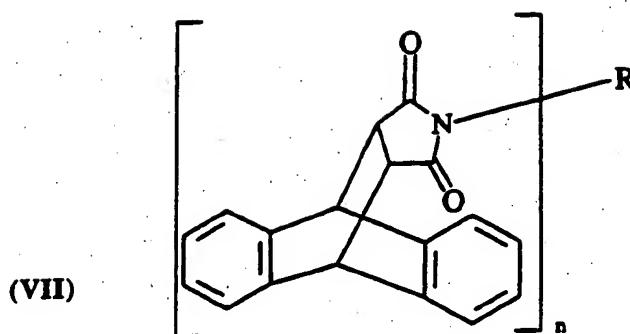
(IV)



(V)



(VI)



in which

R if n=1, is

hydrogen, C<sub>1-24</sub>alkyl (linear or branched), C<sub>5-12</sub>cycloalkyl, C<sub>6-24</sub>aryl,  
C<sub>4-24</sub>heteroaryl, C<sub>7-24</sub>aralkyl, C<sub>7-24</sub>alkaryl, -C<sub>1-24</sub>alkylen-R<sub>7</sub>;

particularly hydrogen, C<sub>1-18</sub>alkyl (linear or branched), C<sub>5-8</sub>cycloalkyl, C<sub>6-18</sub>aryl,  
C<sub>4-18</sub>heteroaryl, C<sub>7-18</sub>aralkyl, C<sub>7-18</sub>alkaryl, -C<sub>1-18</sub>alkylen-R<sub>7</sub>;

preferably hydrogen, C<sub>1-12</sub>alkyl (linear or branched), C<sub>5-8</sub>cycloalkyl, C<sub>6-15</sub>aryl,  
C<sub>4-12</sub>heteroaryl, C<sub>7-18</sub>aralkyl, C<sub>7-18</sub>alkaryl, -C<sub>1-18</sub>alkylen-R<sub>7</sub>;

more preferably hydrogen, C<sub>1-12</sub>alkyl (linear or branched), cyclohexyl, phenyl,  
biphenyl, C<sub>7-12</sub>aralkyl, C<sub>7-12</sub>alkaryl;

if  $n > 1$

$C_{1-24}$ alkylen (linear or branched),  $C_{3-12}$ cycloalkylen,  $C_{6-24}$ arylen,  
 $C_{4-24}$ heteroarylen,  $C_{7-24}$ aralkylen,  $C_{7-24}$ alkarylen;

particularly  $C_{1-18}$ alkylen (linear or branched),  $C_{3-8}$ cycloalkylen,  $C_{6-18}$ arylen,  
 $C_{4-18}$ heteroarylen,  $C_{7-18}$ aralkylen,  $C_{7-18}$ alkarylen;

preferably  $C_{1-12}$ alkylen (linear or branched),  $C_{3-8}$ cycloalkylen,  $C_{6-12}$ arylen,  
 $C_{4-12}$ heteroarylen,  $C_{7-18}$ aralkylen,  $C_{7-12}$ alkarylen;

more preferably  $C_{1-8}$ alkylen (linear or branched), cyclohexylen, phenylen,  
biphenylen,  $C_{7-12}$ aralkylen,  $C_{7-12}$ alkarylen;

$R_1$ ,  $R_2$ ,  $R_3$  are independently selected from hydrogen,  $C_{1-24}$ alkyl (linear or  
branched),  $C_{3-12}$ cycloalkyl,  $C_{6-24}$ aryl,  $C_{4-24}$ heteroaryl,  $C_{7-24}$ aralkyl,  
 $C_{7-24}$ alkaryl, - $NHR_4$ ;

particularly hydrogen,  $C_{1-18}$ alkyl (linear or branched),  $C_{3-8}$ cycloalkyl,  
 $C_{6-18}$ aryl,  $C_{4-18}$ heteroaryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl, - $NHR_4$ ;

preferably hydrogen,  $C_{1-12}$ alkyl (linear or branched),  $C_{3-8}$ cycloalkyl,  
 $C_{6-18}$ aryl,  $C_{7-18}$ aralkyl,  $C_{7-12}$ alkaryl;

more preferably hydrogen,  $C_{1-12}$ alkyl (linear or branched), cyclohexyl,  
phenyl, biphenyl,  $C_{7-12}$ aralkyl,  $C_{7-12}$ alkaryl;

$R_4$  hydrogen,  $C_{1-24}$ alkyl (linear or branched),  $C_{3-12}$ cycloalkyl,  $C_{6-24}$ aryl,  
 $C_{4-24}$ heteroaryl,  $C_{7-24}$ aralkyl,  $C_{7-24}$ alkaryl, - $C_{1-24}$ alkylen- $R_7$ ;

particularly hydrogen,  $C_{1-18}$ alkyl (linear or branched),  $C_{3-8}$ cycloalkyl,  $C_{6-18}$ aryl,  
 $C_{4-18}$ heteroaryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl, - $C_{1-18}$ alkylen- $R_7$ ;

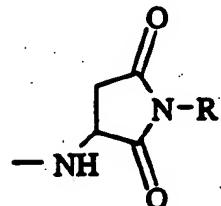
preferably hydrogen, C<sub>1-8</sub>alkyl (linear or branched), C<sub>5-8</sub>cycloalkyl, C<sub>6-18</sub>aryl, C<sub>7-18</sub>aralkyl, C<sub>7-12</sub>alkaryl;

more preferably hydrogen, C<sub>1-8</sub>alkyl (linear or branched), cyclohexyl, phenyl, C<sub>7-12</sub>aralkyl, C<sub>7-12</sub>alkaryl;

R<sub>5</sub>      hydrogen, C<sub>1-24</sub>alkyl (linear or branched), -CH<sub>2</sub>-OH; particularly hydrogen, methyl;

R<sub>6</sub>      -OH, -NHR<sub>4</sub>;

R<sub>7</sub>



X      -CH<sub>2</sub>-, >CH-C<sub>1-4</sub>alkyl- oder -O-; particularly -CH<sub>2</sub>-, >CH-CH<sub>3</sub>, -O-;

n      is an integer selected from 1 to 6, particularly 1 to 4;

m      is an integer selected from 0 to 4, particularly 0 to 2;

The structures are not limited to the isomers drawn in formulae I to VIII.

Compounds of formulae I to VIII are known and can be produced according to well known processes.

Polymeric compositions according to the invention comprise the nucleating agent in an amount of from 0,01 to 5% by weight, preferably from 0,02 to 0,5% by weight, more preferably 0,02 to 0,3% by weight based on the polymeric material.

Another object of the invention is a process to enhance the degree of crystallinity, the

crystallization onset temperature and/or mechanical properties of polymeric materials characterized in that

- in a first step at least one nucleating agent selected from the group consisting of compounds of formulae I to VIII - optionally mixed with other nucleating agents according to the prior art - is added to the unmolten polymeric material and mixed according to known methods forming a mixture,

- in a second step said mixture is melted forming a polymeric composition and

- in a third step said polymeric composition is processed according to known methods

or

- in a first step at least one nucleating agent selected from the group consisting of compounds of formulae I to VIII - optionally mixed with other nucleating agents according to the prior art - is added to the molten polymeric material and mixed according to known methods forming a polymeric composition and

- in a second step said polymeric composition is processed according to known methods.

The invention further relates to the use of special imides according to the above-mentioned formulae I to VIII as nucleating agents for polymeric materials.

Especially suitable as nucleating agents are those of formula I in which

R if n=1, is

hydrogen, C<sub>1-12</sub>alkyl (linear or branched), cyclohexyl, phenyl, biphenyl,  
C<sub>7-12</sub>aralkyl, C<sub>7-12</sub>alkaryl;

if n>1

C<sub>1-8</sub>alkylen (linear or branched), cyclohexylen, phenylen, biphenylen,

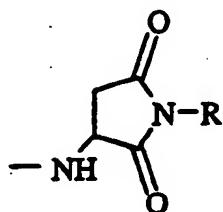
$C_{7-12}$ aralkylen,  $C_{7-12}$ alkarylen;

$R_1$ ,  $R_2$  are independently selected from hydrogen,  $C_{1-12}$ alkyl (linear or branched), cyclohexyl, phenyl, biphenyl,  $C_{7-12}$ aralkyl,  $C_{7-12}$ alkaryl;

$R_4$  hydrogen,  $C_{1-8}$ alkyl (linear or branched), cyclohexyl, phenyl,  $C_{7-12}$ aralkyl,  $C_{7-12}$ alkaryl;

$R_6$  -OH, -NHR<sub>4</sub>;

$R_7$



n is an integer selected from 1 to 4.

The amount of nucleating agent applied is of from 0,01 to 5%, preferably 0,02 to 0,5%, more preferably 0,02 to 0,3% based on the weight of polymeric material present in the composition.

The use of such nucleating agents leads to enhanced physical properties of polymeric compositions, especially for polyolefins, such properties including improved haze, crystallization temperature and mechanical properties.

Further additives that can be added to a polymeric composition according to the invention include antioxidants, such as sterically hindered phenols, secondary aromatic amines or thioethers, such as described in "Kunststoff-Additive"- Gächter/Müller, 3rd Ed., 1990, pp 42-50, the contents of which is incorporated herein by reference; acid scavengers such as sodium-, magnesium- or calcium stearates or -lactates, hydrotalcite, alkoxylated or hydroxylated amines; U.V. stabilizers such as sterically hindered amine (e.g. N-unsubstituted, N-acyl-substituted or N-alkylated 2,2,6,6-tetra-methyl-piperidinyl compounds, also known as hindered amine light stabilizers HALS); U.V. absorbers (e.g.

2-(2'-hydroxy-phenyl)-benztriazoles, 2-hydroxy-benzophenones, 1,3-bis-(2'-hydroxybenzoyl) benzene-salicylates, cinnamates or oxalic acid diamides); U.V. quenchers (e.g. benzoates or substituted benzoates), antistatic agents, flameproofing agents, softeners, plasticizers, lubricants, guard agents, metal deactivators, complexants, biocides, fungicides, other nucleating agents, fillers, pigments and other impact modifiers.

Polymeric materials whose properties can be enhanced by the nucleating agent according to the invention, include homopolymers, copolymers and polymer blends of:

cellulose acetate; cellulose acetobutyrate; cellulose acetopropionate; cresol-formaldehyde resins; carboxymethylcellulose; cellulose nitrate; cellulose propionate; casein plastics; casein-formaldehyde resins; cellulose triacetate; ethyl cellulose; epoxy resins; methyl cellulose; melamine-formaldehyde resins; polyamide; polyamidimide; polyacrylonitrile; polybut-1-ene; polybut-2-ene; polybutylacrylate; poly(butylene-terephthalate); poly(ethyleneterephthalate); polycarbonate; poly(chloro-trifluoro-ethylene); poly(diallylphthalate); polyethylene; chlorinated polyethylene; polyether ketone; polyetherimide; polyethyleneoxide; polyethersulfone; polytetrafluoroethylene; phenol-formaldehyde resins; polyimide; polyisobutylene; polyisocyanurate; polymethacrylimide; polymethylmethacrylate; poly(4-methylpent-1-ene); poly( $\alpha$ -methylstyrene); polyoxy-methylene; polyacetal; polypropylene; polyphenylene-ether; polyphenylenesulphide; polyphenylenesulfone; polystyrene; polysulfone; polyurethane; polyvinylacetate; polyvinylalcohol; polyvinylbutyral; chlorinated polyvinylchloride; polyvinylidenefluoride; polyvinylidenechloride; polyvinylfluoride; polyvinylchloride; polyvinylformaldehyd; polyvinylcarbazole; polyvinylpyrrolidone; silicon polymers; saturated polyesters; urea-formaldehyde resins; unsaturated polyesters; polyacrylates; polymethacrylate; polyacrylamide; maleinate resins; phenolic resins; aniline resins; furane resins; carbamide resins; epoxide resins and silicon resins.

Examples of suitable copolymers include:

acrylonitrile/butadiene/acrylate; acrylonitrile/butadiene/styrene; acrylonitrile/methylmethacrylate; acrylonitrile/styrene/acrylic ester; acrylonitrile/ethylene-propylene-diene/styrene; acrylonitrile/chlorinated polyethylene/styrene; ethylene/propylene; ethylene/propylene-diene;

ethylene/vinylacetate; ethylene/vinylalcohol; ethylene/tetrafluoroethylene; tetrafluoroethylene/hexafluoropropylene; methacrylate/butadiene/styrene; melamine/phenol-formaldehyde; polyester blockamide; perfluoro-alkoxy-alkane; styrene/butadiene; styrene/maleic acid anhydride; styrene/ $\alpha$ -methylstyrene; vinylchloride/ethylene/methacrylate; vinylchloride/ethylene/vinylacetate; vinylchloride/methylmethacrylate; vinylchloride/octylacetate; vinylchloride/vinylacetate and vinylchloride/vinylidenechloride.

Preferred polymeric materials whose properties can be improved by the nucleating agents according to the invention are polyolefins such as polyethylene (e.g. high density polyethylene, low density polyethylene, linear low density polyethylene, or medium density polyethylene), polybutylene, poly-4-methylpentene and copolymers and mixtures/blends thereof as well as polyesters [e. g. poly-(ethylenterephthalate), poly(butylenterephthalate)], polyamides and polyoxymethylene.

The nucleating agents are especially suitable for the use in polyolefins and their copolymers prepared by using processing catalysts known as Generation II to Generation V catalysts and which may or may have not (preferably have not) been subjected to a catalyst removal step.

By the term "catalyst removal step" used herein is meant a step which comprises, for the purpose of actively removing the catalyst residue contained in the polymerized polyolefins, treating the polyolefins with the compounds which can react with the catalyst residue and inactivate or solubilize the residue, such as e.g. alcohols or water and then removing the inactivated or solubilized catalyst residue by physical means such as filtration, washing, and centrifuging.

Thus, in the case of suspension polymerization, the step of separating the resulting polymer from a dispersion medium such as a solvent or a liquified monomer does not fall under the above-mentioned definition of the catalyst residue-removal step, although the catalyst dissolved in the dispersion medium may be removed at the separation step. The step of adding a small amount of catalyst poisons such as ethers, alcohols, ketones, esters and water to the resulting polymer suspension with a gas such as steam or nitrogen to remove the dispersion medium also does not fall under the above-mentioned definition of the catalyst residue-removal step.

What is meant by Generation I catalysts are titanium halide catalysts and an organo aluminium compound or an organo aluminium halide.

What is meant by Generation II catalysts are Generation I catalysts supported on an organo magnesium compound or based on an organo chromium compound supported on SiO<sub>2</sub>.

What is meant by a Generation III catalyst is a Ziegler type complex catalyst supported on a halogen containing magnesium compound.

What is meant by a Generation IV catalyst is a Generation III catalyst with a silane donor.

What is meant by a Generation V catalyst is a bis-indenyl organo titanium compound supported on alumoxane polymers or are bis-cyclopentadienyl-titanium halides activated by aluminium alkyl compounds.

Further generations of highly specific catalysts, especially useful for manufacturing highly stereoregular poly- $\alpha$ -olefins, which are presently under development, belong in the sense of the present invention also to the aforementioned generations of supported catalyst systems. Examples for the microstructure of such highly stereoregular polyolefins are given by syndiotactic polypropylene, isotactic stereoblock polymers, isotactic polypropylene containing steric defects distributed along the polymer chain (so called anisotactic polypropylene) or stereoirregular stereoblock polymers.

Due to the rapid progress in the development of supported newer generation catalyst systems (eg the metallocene catalysts) the commercial significance of these polymers with novel, highly interesting properties increases more and more. However, residues of such further catalyst generations, as long as they contain metals of the 3d, 4d and 5d series of the periodic system supported analogously to the earlier catalyst generations, can also cause disadvantageous properties in the polymer, as long as such residues are not removed physically and are still present in the polymer even in a disactivated form.

These Generations of Catalysts are described in the Twelfth Annual International Conference

on Advances in the Stabilization and Controlled Degradation of Polymers held in Luzern, Switzerland, 21-23 May 1990 in an article on pages 181 to 196 inclusive by Rolf Mülhaupt entitled "New Trends in Polyolefin Catalysts and Influence on Polymer Stability". The contents of this article is incorporated herein by reference and especially Table I on page 184 describing the Generation of Catalysts:

**TABLE I Polyolefin Catalyst Evolution**

| Generation Example             | Cat.   | Act. % | Act. Ti<br>(gPP/gTi h atm) | Stereoreg.<br>(%hept.ins) | Process Technology                         |
|--------------------------------|--|--------|----------------------------|---------------------------|--|
| I $\text{TiCl}_4/\text{AlR}_3$ | 40   | 0.01   |                            | 45%                       | removal of cat. residues<br>and atactic PP |
|                                | $\text{TiCl}_4/\text{AlEt}_2\text{Cl}$                         | 30     | 0.1                        | 92%                       | removal of catalyst residues               |
| II                             | $\text{Mg}(\text{OEt}_2)/\text{TiCl}_4/\text{AlR}_3$           | 40000  |                            | 50%                       | no removal of cat. residues                |
|                                | $\text{SiO}_2/\text{Cp}_2\text{Cr}$                            | 40000  | HDPE                       |                           | (mainly HPDE/LLDPE)                        |
| III                            | Mod. $\text{TiCl}_4$ , cat.                                    | 5000   | 1                          | 95%                       | no purification                            |
|                                | $\text{MgCl}_2/\text{TiCl}_4/\text{AlR}_3$ ,<br>+ ester donor  | 20000  | 10                         | 92%                       |  |
| IV                             | $\text{MgCl}_2/\text{TiCl}_4/\text{AlR}_3$ ,<br>+ silane donor | 40000  | 18                         | 99%                       | no purification<br>no extrusion            |
| V                              | Bis-indenyl- $\text{TiR}_2$ on<br>$(\text{AlCH}_3\text{O})_2$  | 40000  | 100                        | 99%                       | novel PPs, narrow MWD                      |

in which R is an organo group; HDPE is high density polyethylene, LLDPE is linear low density polyethylene, Cp is cyclopentadienyl, Et is ethyl, PP is polypropylene, MWD is molecular weight distribution and x is an integer above 2.

Nucleating agents according to the invention may be added to the polymeric material before, during or after the polymerization step and may be added in solid or molten form, in solution preferably as a liquid concentrate or as a solid masterbatch composition containing 5 to 80% (preferably 10 to 50%) by weight of the nucleating agents and 95 to 20% (preferably 90 to 50%) by weight of a solvent or a solid polymeric material which is identical or compatible with the material to be stabilized.

Nucleating agents according to the invention may be incorporated by known methods into the polymeric material. Of importance is dry-blending of the compositions according to the invention with the polymer fluff or coating shaped polymer particles, e.g. polymers spheres, with the nucleating agents in the form of a molten liquid, a solution or suspension/dispersion. Of particular importance is blending of the compounds with thermoplastic polymers in the melt, for example in a melt blender or during the formation of shaped articles, including films, tubes, fibres and foams by extrusion, injection molding, blow molding, roto-molding, spinning or wire coating. The nucleating agents according to the invention are particularly useful for polypropylene and polyethylene, polyester, polyamide and polyoxymethylene articles of every type.

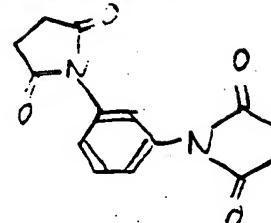
For avoidance of doubt, where a symbol appears more than once in a formula or once in two different formulae, its significances are independent unless indicated to the contrary. Any group capable of being linear or branched is linear or branched unless indicated to the contrary. Further, where a range is given, the figures defining the range are included therein. The abbreviation t-butyl means tertiary butyl, -C(CH<sub>3</sub>)<sub>3</sub>.

Nucleating agents according to the invention improve the thermal and/or mechanical properties of the polymer material without influencing negatively the processing properties of the said polymeric material. But not all properties may be influenced or improved at the same time. This offers the opportunity to modify exactly the properties needed for a certain application by choosing the right nucleating agent. Furthermore the compounds claimed show advantages concerning polymer compatibility over nucleating agents according to the prior art, e. g. the phthalimides claimed in DE 1 951 632.

The invention will now be illustrated by the following examples.

**I. Preparation of the nucleating agents according to the invention**

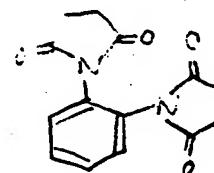
**Example 1**



**Synthesis of 1,3-phenylen-N,N-bis-succinimide**

To a stirred solution of 0.1 mol succinic anhydride in 100 ml acetone at 50°C a solution of 0.05 mol 1,3-phenylenediamine in 60 ml acetone is added during 30 min. After 2 h of additional refluxing the solid is filtered off and dried. It is heated with 2 g sodium acetate and 0.21 moles acetic anhydride for 3 h at 70°C. 100 ml water are added, stirred for 1 h, filtered, washed intensively with hot water and dried. Yield: 72%, mp. 203°C.

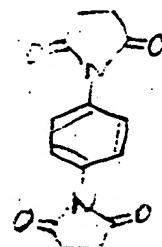
**Example 2**



**Synthesis of 1,2-phenylen-N,N-bis-succinimide**

To a stirred solution of 0.1 mol succinic anhydride in 100 ml acetone at 50°C a solution of 0.05 mol 1,2-phenylenediamine in 60 ml acetone is added during 30 min. After 2 h of additional refluxing the solid is filtered off and dried. It is heated with 2 g sodium acetate and 0.21 moles acetic anhydride for 2 h at 70°C. 150 ml water are added, stirred for 1 h, filtered and recrystallized from hot water and dried. Yield: 32%, mp. >250°C.

**Example 3**



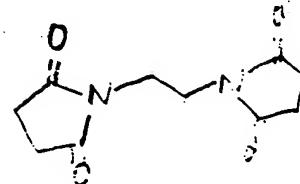
**Synthesis of 1,4-phenylene-N,N-bis-succinimide**

To a stirred solution of 0.2 mol succinic anhydride in 150 ml acetone a solution of 0.1 mol 1,4-phenylenediamine in 50 ml acetone is added during 30 min. After 2 h of additional refluxing the solvent is stripped in vacuo and 2 g sodium acetate and 0.3 moles acetic anhydride are added. The reaction mixture is stirred for 3 h at 70°C, then the separated colorless crystals are collected

on a Büchner funnel, washed with cold water and dried. The raw product is recrystallized from water. Yield: 42%, mp.: 254 - 256°C.

Example 4

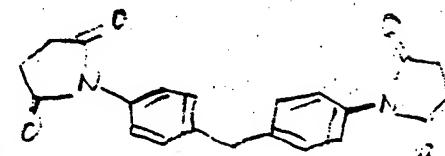
Synthesis of ethylene-N,N-bis-succinimide



To a stirred solution of 0.1 mol succinic anhydride in 50 ml acetone a solution of 0.05 mol ethylenediamine in 50 ml acetone is added during 30 min. After 1 h of refluxing the solid is filtered off and dried. It is heated with 2 g sodium acetate and 0.21 moles acetic anhydride for 2 h at 70°C. 110 ml water are added, stirred for 1 h, filtered and recrystallized from hot water and dried. Yield: 62%, mp. 255°C.

Example 5

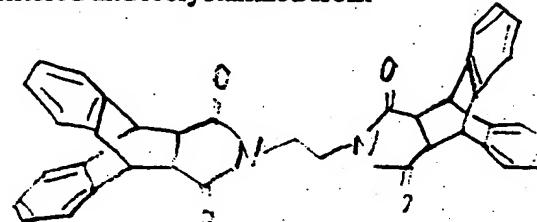
Synthesis of (4,4'-diamino-diphenyl-methane)-N,N-bis-succinimide



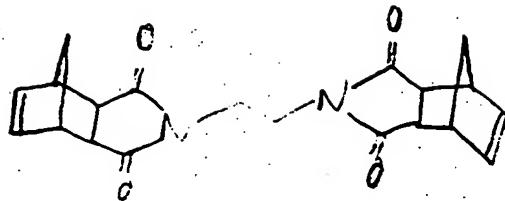
To a stirred solution of 0.1 mol succinic anhydride in 100 ml acetone a solution of 0.05 mol 4,4'-diamino-diphenyl-methane in 50 ml acetone is added during 30 min. After 1 h of refluxing the solid is filtered off and dried. It is heated with 2 g sodium acetate and 0.21 moles acetic anhydride for 2 h at 70°C. 200 ml water are added, stirred for 1 h, filtered and recrystallized from DMF/water and dried. Yield: 68%, mp. 165°C.

Example 6

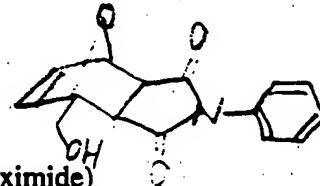
Synthesis of ethylene-N,N-bis-(bicyclo[2.2.2]dibenzo-octadien-dicarboximide)



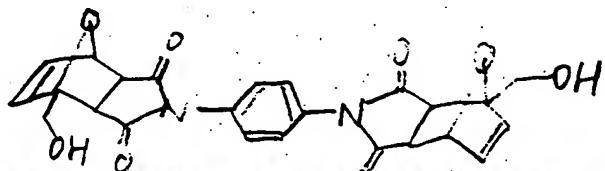
To a stirred solution of 0.1 mol bicyclo[2.2.2]dibenzo-octadien-dicarboxylic anhydride in 200 ml acetone a solution of 0.05 mol ethylenediamine in 50 ml acetone is added during 30 min. After 1 h of reflux 2 g sodium acetate and 0.21 moles acetic anhydride are added and refluxed for 2.5 h. 200 ml water are added, refluxed for 1 h, filtered, recrystallized from dioxane and dried. Yield: 10%, mp. >250°C.

Example 7Synthesis of ethylene-N,N-bis-(norbon-4-en-dicarboximide)

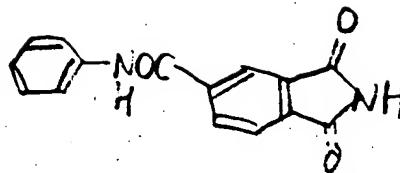
To a stirred solution of 0.1 mol of norbornendicarboxylic anhydride in 100 ml acetone, a solution of 0.05 mols ethylenediamine in 100 ml acetone is slowly added. After refluxing the mixture for 2 h, it is cooled, filtered and dried. This substance is stirred for 2 h at 60°C with a mixture of 2 g sodium acetate and 10 ml acetic anhydride. 50 ml water are added, stirred for 1 h, filtered and dried. The raw product is recrystallized from toluene. Yield: 43%, mp. 244 - 248°C.

Example 8Synthesis of phenyl-N-bis-(1-(hydroxy-methyl)-7-oxo-norbon-4-en-dicarboximide)

To a stirred solution of 0.1 mol maleic anhydride in 150 ml acetone a solution of 0.1 mol aniline in 50 ml acetone is added during 30 min. After 2 h of reflux 2 g sodium acetate and 0.21 moles acetic anhydride are added and refluxed for 2.5 h. 200 ml water are added, refluxed for 1 h, filtered and recrystallized from cyclohexane and dried. This substance is reacted with 0.075 mols furfurylalcohol in 100 ml toluene at 70°C for 12 h. The product is filtered off and recrystallized from ethyl acetate. Yield: 58%, mp. 154°C.

Example 9Synthesis of 1,4-phenylene-N,N-bis-(1-(hydroxy-methyl)-7-oxo-norbon-4-en-dicarboximide)

To a stirred solution of 0.2 mol maleic anhydride in 150 ml acetone a solution of 0.1 mol 1,4-phenylenediamine in 50 ml acetone is added during 30 min. After 1 h of reflux 2 g sodium acetate and 0.21 moles acetic anhydride are added and refluxed for 5 h. 200 ml water are added, refluxed for 1 h., filtered after cooling and recrystallized from DMF and dried. This substance is reacted with 0.1 mol furfurylalcohol in 100 ml toluene at 70°C for 10 h. The product is filtered off and washed with methanol. Yield: 27%, mp. >250°C.

Example 10Synthesis of trimellitic acid imide-anilide

To 0,1 mol of the methyl ester of trimellitic acid imide 0,1 mol aniline and 100 ml decalin is added. The mixture is heated until the theoretical amount of methanol is distilled off (12 h.). After cooling the precipitated product is filtered off and dried. For further purification the raw product is recrystallized from dimethylacetamide. Yield: 86%, mp. >250°C.

Example 11 = Comparative example according to the prior artSynthesis of 1,3-phenylen-N,N-bis-phthalimide

To a stirred refluxing solution of 0,2 mol phthalic anhydride in 200 ml acetic acid a solution of 0,1 mol 1,3-phenylenediamine in 100 ml acetic acid is added during 30 min. After 2 h of additional stirring the off white precipitate is collected on a Büchner funnel, washed neutral with water, acetone and dried. Yield: 62%, mp.: >250°C.

II. Production of the polymeric compositions according to the inventionExamples 12 - 17Polymeric compositions containing

|             |   |
|-------------|---|
| 100.0 parts | 3 <sup>rd</sup> generation random polypropylene copolymer (MFI 7) |
| 0.05 parts  | Irganox <sup>®</sup> 1010   |
| 0.1 parts   | Sandostab <sup>®</sup> P-EPQ                                      |
| 0.1 parts   | calcium stearate  |
| 0.1 parts   | nucleating agent according to table 1 below                       |

are prepared by dry blending the components and extruding this mixture at 210°C on a Händle single screw extruder. The resulting pellets are then injection molded on an Arburg injection

molding machine at 245°C to form plaques of 100 x 100 x 1 mm<sup>3</sup>.

**Examples 18 to 22**

Polymeric compositions containing

|             |   |
|-------------|---|
| 100.0 parts | 3 <sup>rd</sup> generation random polypropylene copolymer (MFI 7) |
| 0.05 parts  | Irganox <sup>®</sup> 1010   |
| 0.1 parts   | Sandostab <sup>®</sup> P-EPQ                                      |
| 0.1 parts   | calcium stearate  |
| 0.3 parts   | nucleating agent according to table 1 below                       |

are prepared according to the procedure given in the examples 12 to 17.

**Examples 23 to 26**

Polymeric compositions containing

|             |   |
|-------------|---|
| 100.0 parts | 3 <sup>rd</sup> generation random polypropylene copolymer (MFI 6) |
| 0.05 parts  | Irganox <sup>®</sup> 1010   |
| 0.1 parts   | Sandostab <sup>®</sup> P-EPQ                                      |
| 0.1 parts   | calcium stearate  |
| 0.1 parts   | nucleating agent according to table 1 below                       |

are prepared according to the procedure given in the examples 12 to 17.

**Examples 27 to 29**

Polymeric compositions containing

|             |   |
|-------------|---|
| 100.0 parts | 3 <sup>rd</sup> generation random polypropylene copolymer (MFI 6) |
| 0.05 parts  | Irganox <sup>®</sup> 1010   |

|           |   |
|-----------|---|
| 0.1 parts | Sandostab® P-EPQ                            |
| 0.1 parts | calcium stearate                            |
| 0.3 parts | nucleating agent according to table 1 below |

are prepared according to the procedure given in the examples 12 to 17.

The following properties are determined:

- the melt flow index of the granules of the polymeric composition after the first extrusion according to ASTM D - 1238-70/L
- the yellowness index of the injection molded plaques according to ASTM D - 1925-70 (reflection)
- the haze values of the injection molded plaques according to ASTM D - 1003/70
- the crystallisation onset temperature (COT). For this purpose samples of about 3 mg are punched out of the middle of the plaques and the COT is determined with a Mettler DSC 20 (200°C to 50°C, -10°C min<sup>-1</sup>).
- The textile strength (TS) according to DIN 53 455:

From the injection molded plaques samples are cut perpendicular to the injection direction. The values for TS given in the tables below are the averages of 5 measurements.

All test results are summarized in the tables 1 and 2.

**Table 1**

**Results of polymeric compositions according to the invention and of a polymeric composition without a nucleating agent**

| Example No. | Nucleating agent of Example | Amount of nucleating agent [parts] | Haze [%] | COT [°C] | TS [N/mm <sup>2</sup> ] |
|-------------|-----------------------------|------------------------------------|----------|----------|-------------------------|
| 12          | 1                           | 0.1                                | 33       | 109      | 26.1                    |
| 13          | 2                           | 0.1                                | 27       | 110      | 27.6                    |
| 14          | 3                           | 0.1                                | 65       | 122      | 27.2                    |
| 15          | 4                           | 0.1                                | 27       | 109      | 25.8                    |
| 16          | 6                           | 0.1                                | 43       | 119      | 25.5                    |
| 17          | -                           | -                                  | 27       | 108      | 24.9                    |
| 18          | 1                           | 0.3                                | 55       | 109      | 25.5                    |
| 19          | 2                           | 0.3                                | 40       | 110      | 24.6                    |
| 20          | 3                           | 0.3                                | 79       | 118      | 27.4                    |
| 21          | 4                           | 0.3                                | 32       | 109      | 26.5                    |
| 22          | 6                           | 0.3                                | 57       | 108      | 24.6                    |

**Table 2**

**Results of polymeric compositions according to the invention and of a polymeric composition without a nucleating agent**

| Example No. | Nucleating agent of Example | Amount of nucleating agent [parts] | Haze [%] | COT [°C] | TS [N/mm <sup>2</sup> ] |
|-------------|-----------------------------|------------------------------------|----------|----------|-------------------------|
| 23          | 7                           | 0.1                                | 23       | 104      | 28.9                    |
| 24          | 8                           | 0.1                                | 22       | 106      | 32.4                    |
| 25          | 9                           | 0.1                                | 24       | 105      | 30.9                    |
| 26          | -                           | -                                  | 26       | 105      | 29.4                    |
| 27          | 7                           | 0.3                                | 25       | 104      | 29.6                    |
| 28          | 8                           | 0.3                                | 30       | 104      | 32.9                    |
| 29          | 9                           | 0.3                                | 55       | 110      | 30.0                    |

Examples 30 to 31 as well as Comparative Examples 32 and 33

Plaques were prepared according to the procedure above, containing

|                  |   |
|------------------|---|
| 100.0 parts      | 3 <sup>rd</sup> generation random polypropylene copolymer (MFI 7) |
| 0.05 parts       | Irganox <sup>®</sup> 1010   |
| 0.1 parts        | Sandostab <sup>®</sup> P-EPQ                                      |
| 0.1 parts        | calcium stearate  |
| 0.1 or 0.3 parts | nucleating agent according to table 1 below                       |

The plaques were stored at ambient temperature. Both samples containing the nucleating agents according to the prior art showed significant blooming out of the nucleating agent already after one week, whereas the plaques containing the nucleating agent according to the invention showed no plate out even after two months.

Table 3 Blooming out - test

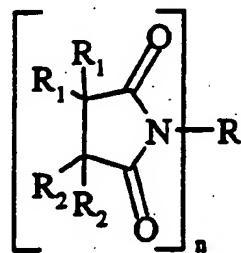
| Example No. | Nucleating agent of example | Amount of nucleating agent [parts] | Blooming out |
|-------------|-----------------------------|------------------------------------|--------------|
| 30          | 1                           | 0.1                                | no           |
| 31          | 1                           | 0.3                                | no           |
| 32          | 11*                         | 0.1                                | yes          |
| 33          | 11*                         | 0.3                                | yes          |

\* Nucleating agent according to the prior art, e. g. DE 1 951 632

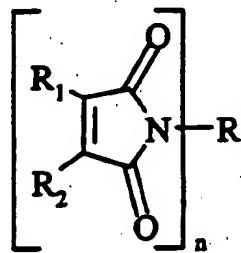
Claims

1. A polymeric composition comprising at least one polymeric material and at least one nucleating agent, characterized in that the nucleating agent is selected from the group consisting of compounds of formulae I to VIII.

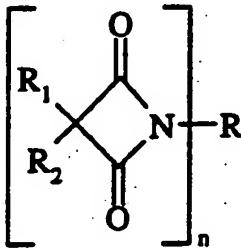
(I)



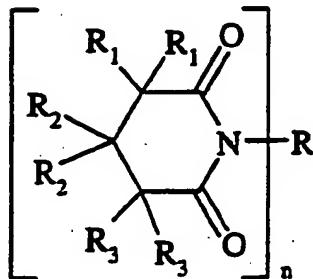
(II)



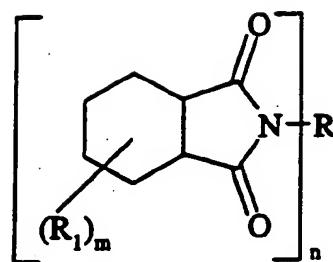
(III)



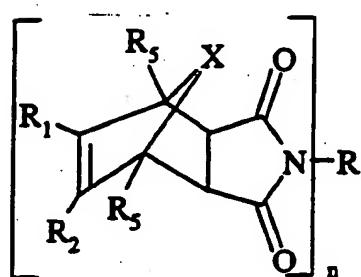
(IV)



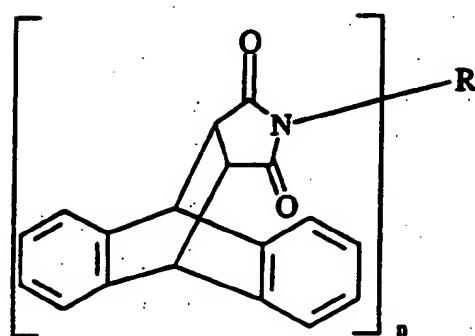
(V)



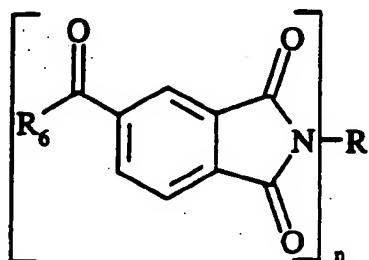
(VI)



(VII)



(VIII)



in which

R if n=1, is

hydrogen, C<sub>1-24</sub>alkyl (linear or branched), C<sub>5-12</sub>cycloalkyl, C<sub>6-24</sub>aryl,

$C_{4-24}$ heteroaryl,  $C_{7-24}$ aralkyl,  $C_{7-24}$ alkaryl, - $C_{1-24}$ alkylen-R<sub>7</sub>;

particularly hydrogen,  $C_{1-18}$ alkyl (linear or branched),  $C_{5-8}$ cycloalkyl,  $C_{6-18}$ aryl,  $C_{4-18}$ heteroaryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl, - $C_{1-18}$ alkylen-R<sub>7</sub>;

preferably hydrogen,  $C_{1-12}$ alkyl (linear or branched),  $C_{5-8}$ cycloalkyl,  $C_{6-18}$ aryl,  $C_{4-12}$ heteroaryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl, - $C_{1-18}$ alkylen-R<sub>7</sub>;

more preferably hydrogen,  $C_{1-12}$ alkyl (linear or branched), cyclohexyl, phenyl, biphenyl,  $C_{7-12}$ aralkyl,  $C_{7-12}$ alkaryl;

if n>1

$C_{1-24}$ alkylen (linear or branched),  $C_{5-12}$ cycloalkylen,  $C_{6-24}$ arylen,  $C_{4-24}$ heteroarylen,  $C_{7-24}$ aralkylen,  $C_{7-24}$ alkarylen;

particularly  $C_{1-18}$ alkylen (linear or branched),  $C_{5-8}$ cycloalkylen,  $C_{6-18}$ arylen,  $C_{4-18}$ heteroarylen,  $C_{7-18}$ aralkylen,  $C_{7-18}$ alkarylen;

preferably  $C_{1-12}$ alkylen (linear or branched),  $C_{5-8}$ cycloalkylen,  $C_{6-18}$ arylen,  $C_{4-12}$ heteroarylen,  $C_{7-18}$ aralkylen,  $C_{7-18}$ alkarylen;

more preferably  $C_{1-8}$ alkylen (linear or branched), cyclohexylen, phenylen, biphenylen,  $C_{7-12}$ aralkylen,  $C_{7-12}$ alkarylen;

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> are independently selected from hydrogen,  $C_{1-24}$ alkyl (linear or branched),  $C_{5-12}$ cycloalkyl,  $C_{6-24}$ aryl,  $C_{4-24}$ heteroaryl,  $C_{7-24}$ aralkyl,  $C_{7-24}$ alkaryl, -NHR<sub>4</sub>;

particularly hydrogen,  $C_{1-18}$ alkyl (linear or branched),  $C_{5-8}$ cycloalkyl,  $C_{6-18}$ aryl,  $C_{4-18}$ heteroaryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl, -NHR<sub>4</sub>;

preferably hydrogen,  $C_{1-12}$ alkyl (linear or branched),  $C_{5-8}$ cycloalkyl,

$C_{6-18}$ aryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl;

more preferably hydrogen,  $C_{1-12}$ alkyl (linear or branched), cyclohexyl, phenyl, biphenyl,  $C_{7-12}$ aralkyl,  $C_{7-12}$ alkaryl;

$R_4$  hydrogen,  $C_{1-24}$ alkyl (linear or branched),  $C_{5-12}$ cycloalkyl,  $C_{6-18}$ aryl,  $C_{4-24}$ heteroaryl,  $C_{7-24}$ aralkyl,  $C_{7-24}$ alkaryl,  $-C_{1-24}$ alkylen-R<sub>7</sub>;

particularly hydrogen,  $C_{1-18}$ alkyl (linear or branched),  $C_{5-8}$ cycloalkyl,  $C_{6-18}$ aryl,  $C_{4-18}$ heteroaryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl,  $-C_{1-18}$ alkylen-R<sub>7</sub>;

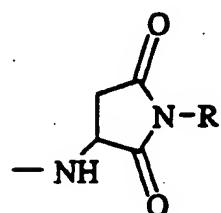
preferably hydrogen,  $C_{1-8}$ alkyl (linear or branched),  $C_{5-8}$ cycloalkyl,  $C_{6-18}$ aryl,  $C_{7-18}$ aralkyl,  $C_{7-18}$ alkaryl;

more preferably hydrogen,  $C_{1-8}$ alkyl (linear or branched), cyclohexyl, phenyl,  $C_{7-12}$ aralkyl,  $C_{7-12}$ alkaryl;

$R_5$  hydrogen,  $C_{1-24}$ alkyl (linear or branched),  $-CH_2-OH$ ; particularly hydrogen, methyl;

$R_6$   $-OH$ ,  $-NHR_4$ ;

$R_7$



$X$   $-CH_2-$ ,  $>CH-C_{1-4}$ alkyl-, oder  $-O-$ ; particularly  $-CH_2-$ ,  $>CH-CH_3$ ,  $-O-$ ;

$n$  is an integer selected from 1 to 6, particularly 1 to 4;

$m$  is an integer selected from 0 to 4, particularly 0 to 2;

2. A polymeric composition according to claim 1 characterized in that the nucleating agent is of formula I in which

R if n=1, is

hydrogen, C<sub>1-12</sub>alkyl (linear or branched), cyclohexyl, phenyl, biphenyl, C<sub>7-12</sub>aralkyl, C<sub>7-12</sub>alkaryl;

if n>1

C<sub>1-8</sub>alkylen (linear or branched), cyclohexylen, phenylen, biphenylen, C<sub>7-12</sub>aralkylen, C<sub>7-12</sub>alkarylen;

R<sub>1</sub>, R<sub>2</sub> are independently selected from hydrogen, C<sub>1-12</sub>alkyl (linear or branched), cyclohexyl, phenyl, biphenyl, C<sub>7-12</sub>aralkyl, C<sub>7-12</sub>alkaryl;

n is an integer selected from 1 to 4.

3. A polymeric composition according to any preceding claim in which the amount of nucleating agent applied is of from 0,01 to 5%, preferably 0,02 to 0,5%, more preferably 0,02 to 0,3% by weight based on the polymeric material.
4. A polymeric composition according to any preceding claim in which the polymeric material is a polyolefin, a polyester, a polyamide, polyoxymethylene, copolymers or blends/mixtures thereof.
5. Process to enhance the degree of crystallinity, the crystallization temperature and/or the mechanical properties of polymeric materials characterized in that
- a) at least one nucleating agent selected from the group consisting of compounds of formulae I to VIII according to claim 1 is added to the unmolten polymeric material and mixed according to known methods forming a mixture
- b) said mixture is melted forming a polymeric composition and

c) said polymeric composition is processed according to known methods

or

a) at least one nucleating agent selected from the group consisting of compounds of formulae I to VIII according to claim 1 is added to the molten polymeric material and mixed according to known methods forming a polymeric composition and

b) said polymeric composition is processed according to known methods.

6. Process according to claim 5 characterized in that the nucleating agent according to claim 2 is added in step a).

7. Process according to any preceding claim 5 or 6 characterized in that the nucleating agent is added in an amount of from 0,01 to 5%, preferably 0,02 to 0,5%, more preferably 0,02 to 0,3% by weight based on the polymeric material.

8. Use of a compound of formulae I to VIII according to claim 1 as nucleating agent for polymeric material.



The  
Patent  
Office

28

Application No: GB 9511702.4      Examiner: Miss M. M. Kelman  
Claims searched: 1 to 8, in respect of Date of search: 10 August 1995.  
formulae (I) and (II)

**Patents Act 1977**  
**Search Report under Section 17**

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C3K KSA KXX

Int Cl (Ed.6): C08K 5/3412, 5/3415, 5/3417, 5/3432, 5/3437

Other: ONLINE:PATENTS

Documents considered to be relevant:

| Category | Identity of document and relevant passage                                  |  | Relevant to claims |
|----------|--|--|--------------------|
| A        | GB 1224721 A   | FARBWERKE HOECHST see whole document   |                    |
| X        | EP 0574804 A2  | BASF see claims 1,5,7,8 and 12 and the Examples                                | 1,3,4,5,6,<br>7,8  |
| &        | US 5362808 A   |  |                    |
| X        | EP 0410514 A1  | AKZO see claims 1,3 and 4 and page 8, lines 24 to 32                           | 1,3,4,5,6,<br>7,8  |
| X        | EP 0373900 A2  | MITSUBISHI PETROCHEMICAL see claims 1 and 4 and page 4, lines 26 to 53         | 1,3,4,5,7,<br>8    |
| X        | EP 0337814 A2  | SUMITOMO see claim 1, page 4, lines 1 to 14 and page 5, lines 27 to 44         | 1,3,4,5,6,<br>7,8  |
| X        | EP 0295103 A2  | SUMITOMO see claims 1 and 2, page 4, lines 33 to 47 and page 6, lines 30 to 36 | 1,3,4,5,6,<br>7,8  |
| X        | US 4311636 A   | BASF see column 6, lines 9 to 21 and Examples 3 and 4                          | 1,2,3,5,6,<br>7,8  |
| A        | WPI Abstract Accession No:71-04536S/03 & DE1935239B(SIEMENS)<br>12.02.1976 |  |                    |

- X Document indicating lack of novelty or inventive step  
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